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Fabrication of SiC/SiC composites by means of *in situ* Crystallization of SiC Fibers

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Abstract

A novel challenge, the *in situ* crystallization of Pre-SiC reinforced-fiber during the fabrication of SiC/SiC composites, has been made for cost effectiveness. Constituent parts of each fabricated material with various manufacturing conditions were assessed by microscopic observation. The depending issues of a prototype process were rather serious that the unwanted areas were conspicuously observed in several places, such as a residual oxide area, unsintered area, coarse matrix, porosity along the fiber-tows, and a huge scale of deformation on fiber-tows. Crystallization process of Pre-SiC fiber itself caused volume contraction about 24.5 %, which result in formation of a gap between the fiber-tow and pyrolytic carbon (PyC) interface. The optimization has been successfully made for a new fabrication technique by controlling most of the known defects. As a result, defects are rarely observed in final product of composite material.

Keywords: SiC/SiC composite, Fabrication, *in situ* crystallization, fiber deformation, porosity

1. Introduction

SiC_f/SiC composites are recognized as prime structural candidates for advanced nuclear energy systems, such as fusion reactors, where SiC/SiC composites must keep excellent physical properties under the severe environments, including high temperature, fast neutron spectrum and surrounding coolant [1-8]. They are at the forefront of advanced material technology because of their low density/weight, high strength and toughness, high temperature capabilities, high wear resistance, excellent chemical and environmental stability, and graceful failure under loading [5-11], contrary to metallic materials, including superalloys which have a restriction in their working temperatures. However, realization of these systems will strongly depend on the optimization of microstructure of SiC/SiC composite regarding the materials and process for constituents; fiber, interface and matrix.

In particular, crystallization of the constituents is emphasized as a technical key issue for fusion reactors [3-7]. In spite of all the superiorities the extremely high cost of SiC/SiC composites are still a significant issue [7-10]. In this study, we have explored a novel challenge to develop a new fabrication route for SiC/SiC composite by employing *in situ* crystallization of all constituents. Microstructure of each of the fabricated conditions had been assessed by scanning electronic microscope (SEM). The objective of this paper is to provide the results of recent trial activities in our group at Kyoto University, aimed at developing a new fabrication route for SiC/SiC composite with the fabrication concepts of a reasonable cost and concise process.

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2. Experimental procedures

Nano-infiltration and transient eutectic-phase (NITE) route has been selected to fabricate a new SiC/SiC composite because of the numerous attractive properties proved by previous works [1-10]. Fabrication of a new SiC/SiC composite was carried out by means of *in situ* crystallization of a pre-SiC fiber.

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2.1. Material preparations

The conventional NITE process used in this work has been described elsewhere [8-10]. Briefly, the cloth was cut into a proper size, slurry-infiltrated with precursor (SiC nano-slurry) of a matrix, and about 14 ply-stacked followed by hot-pressing. SiC nano-slurry is a mixture of SiC nano-powder and

sintering additives ($\text{Al}_2\text{O}_3+\text{Y}_2\text{O}_3$ as 6:4 ratio less than 10 wt %). The fabrication variable is the amount of pyrolytic carbon (PyC) interfaces. SiC/SiC composites were hot-pressed at 1850 °C for 1.5 hr in Ar atmosphere under 20 MPa with the *in situ* crystallization of all constituents, fibers, matrix and pre-pyrolyzed PyC interface. Finally, hot-pressed into a dimension of on demand size, in this study 40×22 mm sized plates were fabricated.

The major difference in fabrication parameter compared with conventional method is fiber coating process. Generally, the CVD coating produces distinct and homogeneous thickness of coating layer, nevertheless it requires a considerable time. Concise processing is inevitable, therefore the focus of fabrication is applying the easiest and cheapest coating as the substitution of the CVD coating, nonetheless, it requires distinct interface between the matrix and fiber. The following procedures are essential to employ a phenolic resin as PyC interface, infiltration of phenolic resin into the fiber tows, thickness control, and pre-pyrolysis of phenolic resin. These processes bring a certain thickness of PyC around the fiber tows. Pre-SiC fiber is a state of polymer driven fiber as a precursor of SiC fiber, which has a strong merit of price competitiveness, despite the mechanical strength is not yet decided. In this study, pre-SiC fiber was employed as a fiber-reinforcement with a pre-pyrolyzed interface of phenolic resin.

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2.2. Design of composite structure

Basic design of composites is 0/90° cross-ply laminate stacking structure, containing about 40 volume fraction of Pre-SiC fibers surrounded by PyC interface. Microstructures of fabricated composites with various amounts of PyC are depicted in figure 1. In prototype LOT#11, the volume fraction of PyC interface was about 3-fold larger than LOT#12. A radical difference of the newly fabricated SiC/SiC composite with high grade composite is that it has SiC matrix with reinforcement of mini-components, which has a constituent of SiC fiber surrounded by PyC interface. Contrarily, high grade composites have on demand thickness of an interface with a flawless infiltration of SiC matrix (see figure 2a). The detailed characteristics of various SiC/SiC composites are shown in table 1.

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2.3. Characterization of fabrication methodology

Microstructural observation was carried out to characterize the fabricated SiC/SiC composites. Densitometry test was fulfilled by the Archimedean method to examine the density and content of porosity

after manufacture [8]. Digital image analysis was used to confirm the microstructural defects focused on deformation and porosity generation of crystallized fibers. Microstructural analysis was performed on each fabrication condition of SiC/SiC composites with the control of the PyC amount. Above all, the amount of PyC is controlled by the weight of used phenolic resin, and then measured by the weight of pyrolyzed PyC. It is quantitatively hard to control it, due to the weight loss in various handling and processing. The pre-pyrolysis process in a vacuumed chamber does not provide the homogeneous amount of coating around the fiber-tows. Some of the excess amounts are eliminated before applying as fiber-reinforcement. However, the exact volume fraction is measured and calculated by the digital image analysis.

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3. Results and discussion

Microstructures of newly fabricated composites are shown in figure 1, which show the amount of employed PyC in an intra-bundle of fibers. Results of the digital image analysis show that PyC volume of LOT#11 was 1.74 and 1.45 times more than LOT#17 and LOT#12 (see figure 1 d-f). The SEM image in back scattered electron imaging (BEI) mode indicates fibers and PyC in color of gray and black, respectively. Severe fiber deformation and micro-pore formation are observed in prototype LOT#11. Volume fraction of PyC was about 4.4-fold larger in case of the more flawed region where many defects are. Increase of PyC amount results in severe fiber deformation and/or pore generation, which plays an important role on mechanical properties. Matrix infiltration in an intra-bundle was hardly observed. Consequently, reinforcement of the PyC interfaced SiC fiber bundles as a mini-component around SiC matrix was fabricated.

[LF]

3.1. Observed defects in prototype composites

Porosity in prototype materials was mainly generated in two forms (see figure 2b, 3a and 4), one is pore in a matrix and another is an aperture around the fiber which causes separation of fiber-tows. Dominant reason of porosity were excess pressure and stress concentration caused by non-uniform PyC coating around the fibers depicted as figure 5 and the volume contraction of fiber itself during the crystallization process of Pre-SiC fiber (see figure 2 and 3). These porosities influenced on bonding strength, which gradually weaken the mechanical strength [7-10].

Fiber deformation of LOT#11 was comparatively serious, the results of image analysis show that

the volume contraction ratio was around 24.5 %. The deformation ratio, defined as fiber length of pressure perpendicular over pressure normal, was around 2.44 in case of oval shape; it means that there will be quite a lot geometrical discordance and generation of pore in the form of the apertures around the fiber (see figure 3a). Interface cleavages were conspicuously observed in prototype materials but LOT#17 (see figure 3). In LOT#17, micro pores and interface cleavage were hardly observed due to the adequate amount of employed PyC (see figure 3b). It was clarified in other works that, a unit of detachment was relatively larger when crack propagation connects to the next cleavage side by side [8-10]. As the consequence, strength degradation was measured both by pore in the matrix and aperture along the fiber-tows, caused by weak bonding strength between the constituents [8-10].

Other defects were conspicuously observed in prototype materials, that is to say, various chances of improvement were observed while examining the prototype materials. The depending issues of the prototype process were rather serious. Therefore, as illustrated in figure 4, the process optimization has been done on following issues (a) Irregular deformation caused by non-uniform PyC coating, (b) Excess pressure and stress concentration causing serious fiber deformation, (c) Easy fiber detachment due to the weak bonding strength between fiber and interface, (d) Inadequate densification in a matrix, (e) Distribution of remained oxide in a matrix, (f) Melted oxide phase around the interface, (g) Conspicuous micro-pores, and (h) Severe cleavage and deformation in PyC interface.

[LF]

3.2. Densification of composites

As illustrated in table 2, near-full densification on the final product was achieved by controlling the most known defects. Mainly, the defects were resulted from the excess amount of pre-pyrolyzed PyC. The nonhomogeneous thickness of pre-pyrolyzed PyC around the fiber-tows results in stress concentration during the sintering process. The stress concentration also provokes the severe deformation of fiber-tows and interface cleavage as shown in figure 5. Above mentioned deficiencies noticeably observed in prototype materials, but not in the final product due to the appropriate control of PyC amount. Melted-flowed excess oxides shown in figure 5 were observed in all fabricated composites, which require more fabrication improvements. However, the optimization have been successfully made for a new fabrication technique by controlling most of known defects; as a result, the known defects are rarely observed in final product LOT#17 (see figure 3b and figure 5b).

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4. Summary

Improvements have been successfully accomplished for the new fabrication technique by controlling most of the formally-described defects in the prototypes. As a result, in the microstructure of final product, the known defects are rarely observed.

The crucial defects are porosity in the form of pore and aperture, fiber deformation, and interface cleavage, which weaken the mechanical strength. Because the disproportional pressure delivered to each area where contains different fiber volume fraction and non-uniform PyC interface; a huge scale of fiber deformation was observed around the deformation ratio of 2.4. Aperture along the fiber was generated by the volume contraction of Pre-SiC fiber itself in the process of crystallization during the hot-pressing where pressure delivery hardly occurred. Consequently, it provokes weak bonding strength, which shows a deleterious effect on a mechanical strength.

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Table 1 Characteristics of the SiC/SiC composites by various fabrication routes.

SiC/SiC composites	Fabrication route	Fiber coating method	Fiber type	PyC interface*
Prototype (LOT#11)	NITE	Pre-pyrolysis	Pre-SiC fiber	1.7–7.5
Prototype (LOT#12)	NITE	Pre-pyrolysis	Pre-SiC fiber	1.5–2.5
Final product (LOT#17)	NITE	Pre-pyrolysis	Pre-SiC fiber	1
Commercial material #1	NITE	CVD	Cef-NITE	500 nm thickness
Commercial material #2	CVI	CVD	Tyranno SA	80 nm thickness

*Relative amount of employed pyrolytic carbon (PyC) is measured for fabricated composites, which divided by the amount used in LOT#17 as a reference. The value varies according to the measured area within the range.

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Table 2 Densimetry property of fabricated materials.

	LOT#17	LOT#12	LOT#11
Apparent density [g/cm ³]	3.08	2.89	2.77
Bulk density [g/cm ³]	3.06	2.74	2.66
Open porosity [%]	0.50 ± 0.03	5.08 ± 0.04	4.20 ± 0.04

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Figure captions

Fig. 1 A typical region normal to the fiber direction, which show employed amount of PyC in fabricated materials of a) LOT#17, b) LOT#12, and c) LOT#11. An example of digital image analysis is shown in bottom (d-f). Back scattered electron imaging mode indicates fibers and PyC in color of gray and black, respectively. Bottom images represent a sample of digital image analysis to calculate the actual amount of volume fraction.

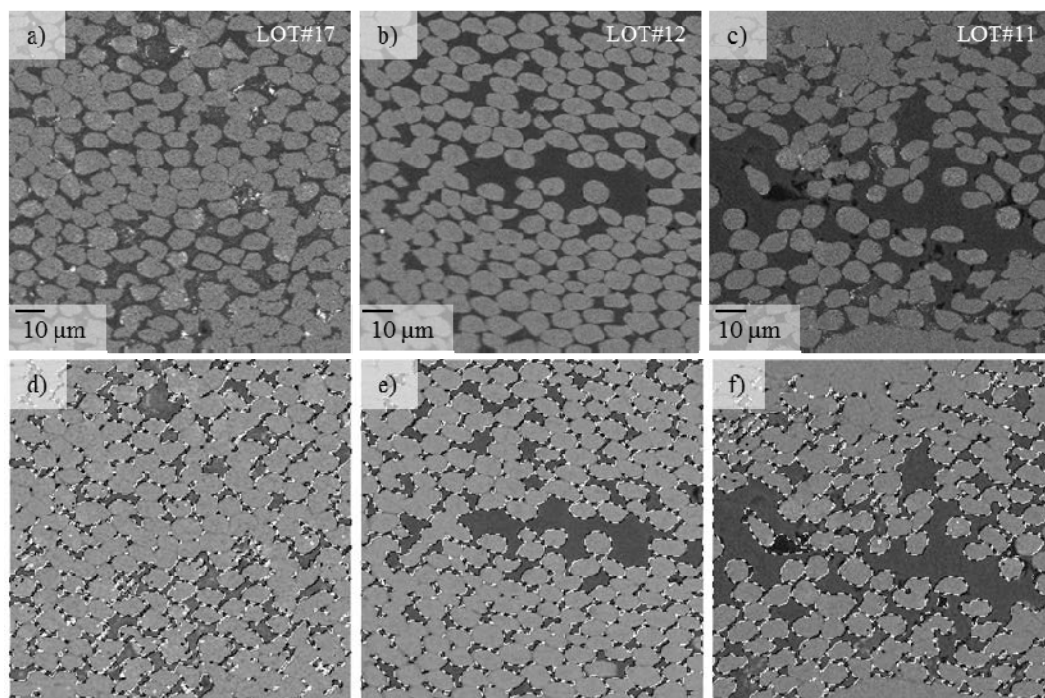
Fig. 2 Cross-sectional images of SiC/SiC composites by (a) near-full dense NITE route, and (b) new fabrication route shows the aperture around the fiber-tow.

Fig. 3 Microstructures of newly fabricated materials (a) deformed fibers and crack generation during hot-pressing in material LOT#11, and (b) near full-dense level of material LOT#17.

Fig. 4 Conspicuous defects in a typical region of prototype material LOT#11. (a, and b) irregular deformation, (c) fiber-tow separation, (d) coarse matrix, (e) excess additives, (f) excess oxides, (g) micro-pores, and (h) PyC cleavage.

Fig. 5 Cross sectional images of fabricated material (a) LOT#11 shows the stress concentration due to the nonhomogeneous thickness of pre-pyrolyzed PyC, and (b) LOT#17.

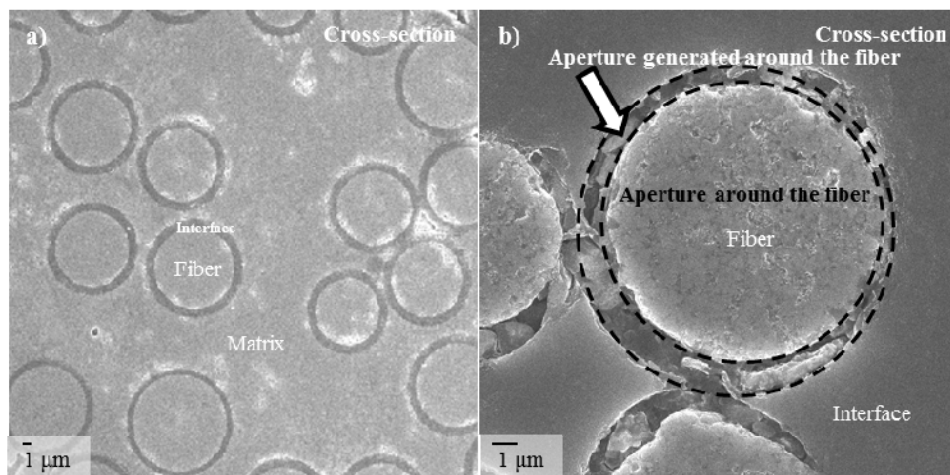
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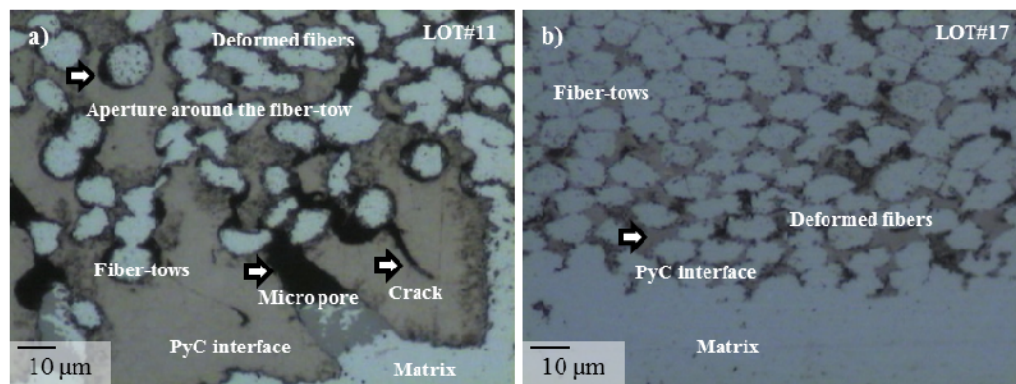
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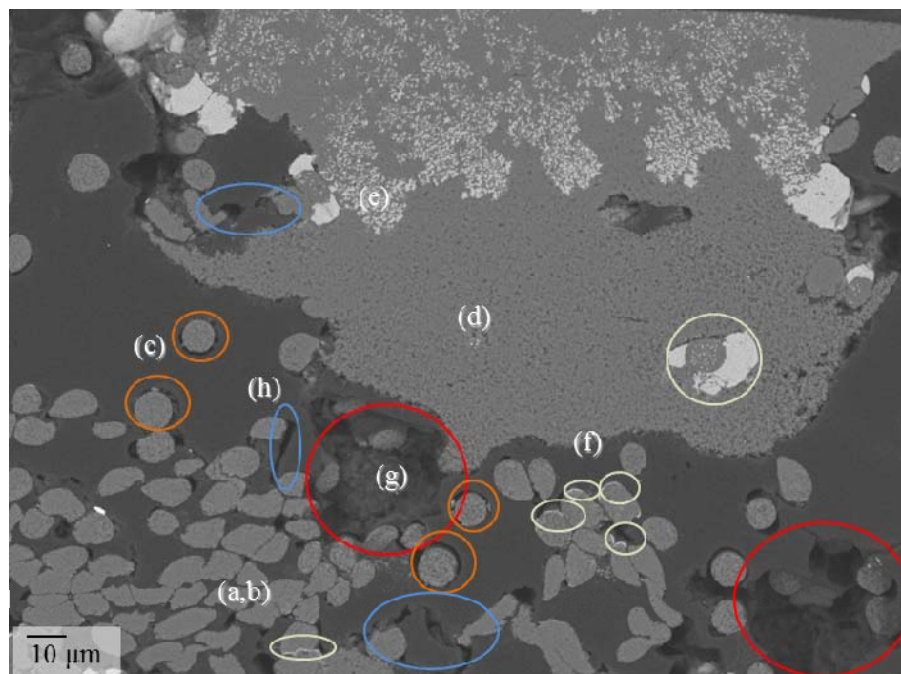
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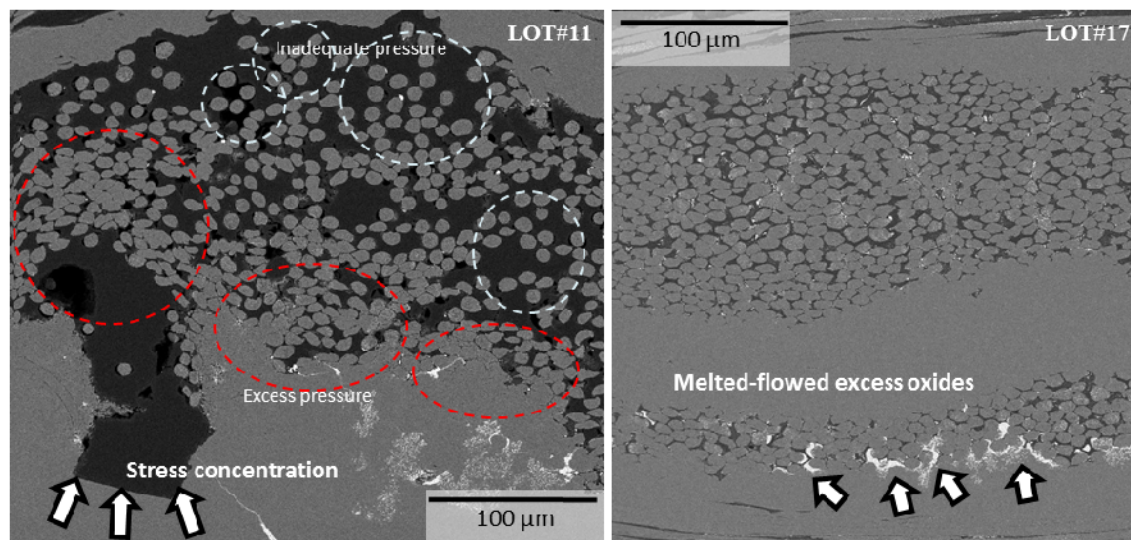
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